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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.028
 wR factor = 0.075
Data-to-parameter ratio = 22.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetra-*n*-butylammonium μ -bromo-di- μ -cyclohexane-thiolato-bis[tricarbonylmolybdenum(I)]

The reaction of $[\text{Mo}_2(\text{SC}_6\text{H}_{11})_2(\text{CO})_8]$ and $(\text{C}_4\text{H}_9)_4\text{NBr}$ in acetone affords a new dinuclear molybdenum(I) complex, $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Mo}_2\text{Br}(\text{C}_6\text{H}_{11}\text{S})_2(\text{CO})_6]$. The crystal structure revealed the MoS_2Mo core to be planar; the Br atom coordinates to two Mo atoms, forming another bridge.

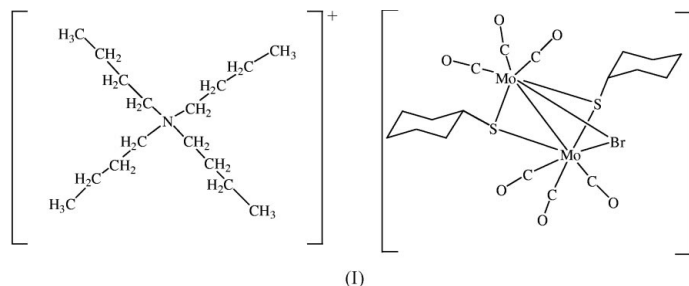
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Comment

The chemistry of complexes containing low-valence metal atoms has increasingly attracted the attention of chemists and bioinorganic chemists. Since the dinuclear molybdenum(0) thiolate carbonyl complexes (Lu *et al.*, 1983, Bose *et al.*, 1986, Eldredge *et al.*, 1988) $[\text{Mo}_2(\text{CO})_8(\text{SR})_2]^{2-}$ ($R = \text{Ph}$, 'Bu) were synthesized and their interesting two-electron-transfer character was revealed by Zhuang *et al.* (1984), a systematic investigation of the synthesis, structure and properties of this type of complex, including the molybdenum(I) analogs, has been developed by our research group (Zhuang *et al.*, 1985, 1986, 1996).



Recently, we introduced the chair-form cyclohexanethiolate (SC_6H_{11}) ligand to these molybdenum compounds (Zhou *et al.*, 2002), with the aim of preparing new Mo^{I} compounds by introducing different functional ligands into $[\text{Mo}_2(\text{SC}_6\text{H}_{11})_2(\text{CO})_8]$, then determining their structures and measuring their properties. We report here the synthesis and structure of the title compound, (I), obtained from the reaction of $(\text{C}_4\text{H}_9)_4\text{NBr}$ with $[\text{Mo}_2(\text{SC}_6\text{H}_{11})_2(\text{CO})_8]$.

The molecular structure of the anion of (I) is shown in Fig. 1. Each Mo atom has a distorted octahedral geometry, coordinated by three C carbonyl atoms, two S atoms from SC_6H_{11} bridging groups and one Br atom. Two *fac*- $\text{Mo}(\text{CO})_3$ fragments are linked together by two SC_6H_{11} and one Br ligand, forming a mixed triple-bridged dimer, which is an edge-sharing bioctahedral structure. The Mo_2S_2 unit in (I) is essentially planar, as also seen in $[\text{Mo}_2(\text{SC}_6\text{H}_{11})_2(\text{CO})_8]$. Two chair-form C_6H_{11} ligands on the S atoms are on the same side of the Mo_2S_2 plane, resulting in a *syn* configuration, with the Br ligand lying on the other side of this plane. The Mo—C distances *cis* to Br1 [$\text{Mo1}-\text{C2} = 1.927$ (2) Å and $\text{Mo2}-\text{C4} =$

1.921 (2) Å] are shorter than those *trans* [Mo1—C1 = 2.022 (2) Å Mo1—C3 = 2.020 (2) Å, Mo2—C5 = 2.029 (2) Å and Mo2—C6 = 2.023 (2) Å] to the Br ligand. It is worth noting that the Mo···Mo distance of the title compound [Mo1···Mo2 = 2.8635 (13) Å] is shorter than that of [Mo₂(SC₆H₁₁)₂(CO)₈] [Mo···Mo = 2.975 (1) Å], probably because of the bridging Br atom.

Experimental

All the reactants and solvents were degassed before use and all the procedures were carried out under a nitrogen atmosphere. [Mo₂(SC₆H₁₁)₂(CO)₈] (0.196 g, 0.30 mmol) was dissolved in acetone (15 ml). To this green solution was added an equivalent of (C₄H₉)₄NBr (0.098 g, 0.30 mmol); the solution immediately turned brown, accompanied by vigorous CO evolution. The reaction mixture was stirred at 323 K overnight, yielding a brown solution, which was evaporated under vacuum to 5 ml. 2-Propanol (10 ml) was added and the resulting solution was filtered and allowed to stand at 277 K for several days to obtain crystals for X-ray single-crystal diffraction analysis. The resulting gray precipitate was washed with acetonitrile and dried under vacuum to yield 0.127 g of pure product (46% yield based on the [Mo₂(SC₆H₁₁)₂(CO)₈] used).

Crystal data

(C₁₆H₃₆N)[Mo₂Br(C₆H₁₁S)₂(CO)₆] $D_x = 1.452 \text{ Mg m}^{-3}$
 $M_r = 912.72$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1/n$ Cell parameters from 9089 reflections
 $a = 10.738 (5) \text{ \AA}$ $\theta = 3.0\text{--}27.5^\circ$
 $b = 19.953 (10) \text{ \AA}$ $\mu = 1.70 \text{ mm}^{-1}$
 $c = 19.498 (9) \text{ \AA}$ $T = 293 (2) \text{ K}$
 $\beta = 91.863 (5)^\circ$ Prism, gray
 $V = 4175 (3) \text{ \AA}^3$ $0.70 \times 0.30 \times 0.25 \text{ mm}$
 $Z = 4$

Data collection

Rigaku Mercury CCD 9485 independent reflections
 diffractometer 8809 reflections with $I > 2\sigma(I)$
 ω and φ scans $R_{\text{int}} = 0.019$
 Absorption correction: multi-scan $\theta_{\text{max}} = 27.5^\circ$
 (CrystalClear; Rigaku/MS, $h = -13 \rightarrow 13$
 2004) $k = -25 \rightarrow 25$
 $T_{\text{min}} = 0.529$, $T_{\text{max}} = 0.654$ $l = -25 \rightarrow 23$
 31610 measured reflections

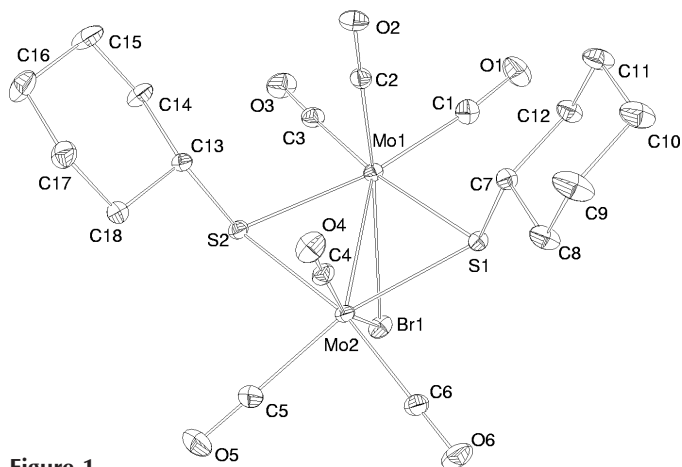


Figure 1
 The structure of the anion of the title complex, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 2.1794P]$
 $R[F^2 > 2\sigma(F^2)] = 0.028$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.075$ $(\Delta/\sigma)_{\text{max}} = 0.003$
 $S = 1.04$ $\Delta\rho_{\text{max}} = 1.19 \text{ e \AA}^{-3}$
 9485 reflections $\Delta\rho_{\text{min}} = -0.78 \text{ e \AA}^{-3}$
 419 parameters
 H atoms treated by a mixture of independent and constrained refinement

Table 1

Selected geometric parameters (Å, °).

Mo1—C2	1.927 (2)	Mo2—C4	1.921 (2)
Mo1—C3	2.020 (2)	Mo2—C6	2.023 (2)
Mo1—C1	2.022 (2)	Mo2—C5	2.029 (2)
Mo1—S1	2.4605 (9)	Mo2—S2	2.4593 (9)
Mo1—S2	2.4718 (9)	Mo2—S1	2.4699 (9)
Mo1—Br1	2.7831 (9)	Mo2—Br1	2.7654 (8)
Mo1—Mo2	2.8635 (13)		
Mo2—Br1—Mo1	62.14 (3)	Mo2—S2—Mo1	71.00 (3)
Mo1—S1—Mo2	71.01 (3)		

H atoms were positioned geometrically, assigned isotropic displacement parameters and allowed to ride on their respective parent C atoms [C—H = 0.93–0.98 Å; $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 times $U_{\text{eq}}(\text{C})$]. The highest electron-density peak is located 0.05 Å from atom Mo1.

Data collection: *CrystalClear* (Rigaku/MS, 2004); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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